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Organonickel(II) Complexes Containing Carbon-bonded Heterocycles as a Ligand

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Oxidative addition reactions of 2- and 3-chloropyridines and of 2-chloropyrazine to tetrakis(triphenylphosphine)nickel(0) occurred in toluene at ambient temperature to afford dinuclear nickel(II) complexes containing carbon-bonded heterocycles as a ligand. They are quite stable and the bridging chloride was readily substituted by other halides and pseudohalides preserving the dinuclear structure. 8-Chloroquinoline yielded a mononuclear complex as an exception. These novel organonickel(II) complexes were characterized by analytical and molecular weight data together with IR, ^{1}H NMR, and ^{13}C NMR spectra. Di-μ-chloro-bis(2-pyridyl)bis(triphenylphosphine)dinickel(II) was found to be an excellent catalyst for selective cross coupling of 2-chloropyridine with methylmagnesium bromide.

Organonickel complexes have attracted interest of many investigators in coordination chemistry, synthetic chemistry, and other related fields.[1] The transition metal–carbon bond is not so unstable as was formerly considered. Thus the *trans*-NiX(aryl)$(PR_3)_2$ complexes, which are prepared conveniently by the oxidative addition reactions of aryl halides with tetrakis(tertiary phosphine)nickel(0),[2] are stable especially when the aryl ligand bears an *ortho*-substituent.[3] Benzyl,[4] vinyl, and acyl[5] halides also react with the nickel(0) complexes to afford similar square-planar organonickel(II) complexes which are isolable though they are less stable than the aryl complexes.

Cross coupling of alkyl, aryl, and alkenyl Grignard reagents with aryl and alkenyl halides was found by Kumada and his coworkers to be catalyzed by the dichlorodiphosphinenickel(II) complexes and the diorganonickel(II) complexes were presumed to be important intermediates.[6] The efficient method of carbon–carbon bond formation was successfully applied to halogenopyridines.[7] The σ-pyridyl nickel(II) complexes must be included in the catalytic turn-over in these reactions, although they have not yet been isolated.

Only a few examples of the carbon-bonded pyridyl complexes with transition metals have been reported. Stable (2-pyridyl)pentacyanocobaltate(III) was obtained by the reaction between 2-iodopyridine with pentacyanocobaltate(II).[8] Reactions of perfluoropyridine with several metal carbonyl compounds afforded the perfluoro-4-pyridyl complexes.[9] 2-Pyridylgold(I) was obtained by the reaction of chloro(triphenylarsine)gold(I) with 2-pyridyllithium and assumed to be a cyclic trimer.[10] 2-Methyl-, 2-phenyl-, and 2-vinylpyridines reacted with bis(η-cyclopentadienyl)methyltitanium(III) to give a 6-pyridyl complex, in which the nitrogen atom also interacts with the metal atom to form a three-membered titanocycle.[11] This paper reports very stable nickel(II) complexes containing carbon-bonded pyridines and two other nitrogen heterocycles as a ligand.

Experimental

Unless otherwise stated, air-sensitive materials were handled under a nitrogen atmosphere. Solvents were distilled under nitrogen and other reagents purged with nitrogen before use. Tetrakis(triphenylphosphine)nickel(0) and tetrakis(triphenyl phosphite)nickel(0) were prepared by the methods of Schunn,[12] and McLaughlin.[13] 2-Pyridyllithium was prepared according to Gilman and Spatz,[14] and sodium acetylacetonate by the reaction of acetylacetone with metallic sodium in methanol. Halopyridines, tertiary phosphines, and Grignard reagents were purchased and used without further purification.

Preparation of Di-μ-halogeno-bis(2-pyridyl)bis(triphenylphosphine)dinickel(II) Complexes, $[NiX(C_5H_4N\text{-}C^2)(PPh_3)]_2$, *where* X=Cl (**1a**), Br(**1b**), *and* I(**1c**). To a solution of tetrakis(triphenylphosphine)nickel(0) (2.5 g, 2.3 mmol) in toluene (100 ml) was added dropwise 2-chloropyridine (0.46 g, 4.0 mmol) or 2-bromopyridine (0.58 g, 3.7 mmol). The reaction proceeded quickly at ambient temperature to deposit an orange-red precipitate. After stirring for 3 h, the product was filtered, washed with methanol, and dried *in vacuo*. The yields were 60% for **1a** and 55% for **1b**. The crude product (*ca.* 0.4 g) of **1a** or **1b** was dissolved in dichloromethane (10 ml). After filtration, methanol (*ca.* 40 ml) was added slowly to the filtrate to precipitate glittery brownish yellow crystals, which were filtered, washed with diethyl ether, and dried *in vacuo*.

Compound **1c** was prepared by metathesis of **1a**. Compound **1a** (0.5 g, 0.6 mmol) was dissolved in dichloromethane (30 ml), and methanol (15 ml) was added slowly to the solution. A methanol solution (15 ml) of an excess amount (1.8 g, 12 mmol) of sodium iodide was then added slowly and the mixture was stirred for 2 h at room temperature. After evaporation of the solvent under reduced pressure, the concentrate (*ca.* 20 ml) was left standing for 2 h. An orange-red precipitate of **1c** was filtered and washed with methanol several times and with diethyl ether. The yield was 80%. Complex **1b** was also derived from **1a** by the same method in a 90% yield.

Preparation of Di-μ-chloro-bis(6-chloro-2-pyridyl)- and Di-μ-chloro-bis(5-chloro-3-pyridyl)-bis(triphenylphosphine)dinickel(II) Complexes, $[NiCl(R)(PPh_3)]_2$, *where* $R{=}C_5H_3(6\text{-}Cl)N\text{-}C^2$ (**2a**) *and* $C_5H_3(5\text{-}Cl)N\text{-}C^3$ (**2b**). The reaction of tetrakis(triphenylphosphine)nickel(0) (2.5 g, 2.3 mmol) with 2,6- or 3,5-dichloropyridine (1.5 g, 10 mmol) was carried out in toluene (140 ml) at ambient temperature in a similar manner as above. After stirring for 5 h, compound **2a** was obtained as an orange-red precipitate in a 90% yield. The reaction for **2b** was remarkably slow and allowed to proceed for 3 d to deposit a brown precipitate in a 70% yield.

Preparation of Di-μ-chloro-bis(3-pyridyl)-, Di-μ-chloro-bis(2-pyrazinyl)-, and Di-μ-chloro-bis(6-methoxy-2-pyridyl)-bis(triphenylphosphine)nickel(II) Complexes, $[NiCl(C_5H_4N\text{-}C^3)(PPh_3)]_2$ (**3**), $[NiCl(C_4H_3N_2\text{-}C^2)(PPh_3)]_2$ (**4**), *and* $[NiCl(C_5H_3\text{-}(6\text{-}CH_3O)\text{-}N\text{-}C^2)(PPh_3)]_2$ (**5**). Compounds **3**, **4**, and **5** were prepared by the method analogous to that for **1a**. The reaction finished within 1 h in the case of **4** and **5**, but it took about 24 h for **3**. Yields of crude products were 40, 90, and 80% for **3**, **4**, and **5**, respectively. On recrystallization from dichloromethane–methanol **3** and **5** were obtained as orange-yellow crystals and **4** was orange-red. Compound **3** is less stable in air and prompt handling is necessary.

Preparation of Chloro(8-quinolyl)bis(triphenylphosphine)nickel(II), [$NiCl(C_9H_6N\text{-}C^8)(PPh_3)_2$]. A toluene solution (40 ml) of 8-chloroquinoline (1.6 g, 10 mmol) was added drop by drop to a solution of tetrakis(triphenylphosphine)nickel(0) (2.5 g, 2.3 mmol) in toluene (100 ml). After stirring for 3 h, a yellow precipitate was filtered, washed with diethyl ether, and dried *in vacuo*. The yield was 90%.

Preparation of Di-μ-pseudohalogeno-bis(6-substituted 2-pyridyl)-bis(triphenylphosphine)dinickel(II) Complexes, [$NiX(R)(PPh_3)$]$_2$, *where* $R=C_5H_3(6\text{-}CH_3O)N\text{-}C^2$, $X=N_3$ ***(7a)***, *OCN* ***(7b)***, *SCN* ***(7c)***, *and SeCN* ***(7d)***; $R=C_5H_3(6\text{-}Cl)N\text{-}C^2$, $X=N_3$ ***(7a′)***, *OCN* ***(7b′)***, *and SCN* ***(7c′)***. Complex **5** or **2a** (0.4 g, 0.4 mmol) was dissolved in dichloromethane (40 ml) and methanol (15 ml) was added slowly to the solution. A methanol solution (15 ml) of sodium azide (0.3 g, 4 mmol), sodium cyanate (0.3 g, 4 mmol), sodium thiocyanate (0.3 g, 4 mmol), or potassium selenocyanate (0.6 g, 4 mmol) was added drop by drop to the complex solution. (Sodium cyanate was dissolved in 5 ml of water and then methanol was added to make up a 15 ml solution.) After stirring for 2 h, the reaction mixture was concentrated to about 20 ml by evaporation under reduced pressure to deposit an orange-yellow or orange-red precipitate in 65 (**7a**), 75 (**7b**), 90 (**7c**), 47 (**7d**), 70 (**7a′**), 75 (**7b′**), and 92% (**7c′**) yields, respectively. Glittery crystals of each complex were obtained by recrystallization from dichloromethane–methanol.

Preparation of Bis(acetylacetonato)bis(6-chloro-2-pyridyl)dinickel(II), [$Ni(C_5H_3(6\text{-}Cl)N\text{-}C^2)(acac)$]$_2$ ***(8)***. Complex **2a** (0.5 g, 0.5 mmol) was dissolved in dichloromethane (30 ml) and methanol (10 ml) was added slowly to it. A methanol solution (15 ml) of sodium acetylacetonate was added dropwise to the complex solution. After stirring for 7 h, the reaction mixture was concentrated to 20 ml by evaporation at ambient temperature under reduced pressure, and left standing for 30 min. A precipitate was separated by filtration and dissolved in dichloromethane (10 ml) and a blue insoluble residue was filtered off. Methanol (30 ml) was added to the filtrate and the solution was again evaporated to 20 ml to deposit yellow-orange crystals in a 60% yield. The blue residue was identified as sodium tris(acetylacetonato)-nickelate(II) (yield, 7%) on the basis of elemental analysis and IR spectrum.

Reaction of Compound ***8*** *with Triphenyl Phosphite.* Triphenyl phosphite (1.0 g, 3 mmol) was added to a suspension of compound **8** (0.3 g, 0.6 mmol) in methanol (40 ml) and the mixture was heated under reflux for 3 h. A precipitate was filtered off during hot and the filtrate was concentrated to 20 ml under reduced pressure and allowed to stand for 2 d to deposit a white precipitate of 6,6′-dichloro-2,2′-bipyridine. The product was dissolved in dichloromethane (5 ml) and methanol (20 ml) was added to the solution to separate out a less soluble contaminant. This procedure of purification was repeated several times to remove a small amount of tetrakis(triphenyl phosphite)nickel(0) (Found: C, 66.04; H, 4.81%. Calcd for $C_{72}H_{60}P_4O_{12}Ni$: C, 66.53; H, 4.65%). The yield of the coupling product was 60%. Found: C, 53.03; H, 2.66; N, 12.33%; parent mass peak (*m/e*), 223.90. Calcd for $C_{10}H_6N_2Cl_2$: C, 53.36; H, 2.69; N, 12.45%; *m/e*, 223.90.

Cross Coupling of Methylmagnesium Bromide to 2-Chloropyridine Catalyzed by Compound ***1a***. Compound **1a** (0.7 g, 0.9 mmol) was added to a tetrahydrofuran (THF) solution (100 ml) of 2-chloropyridine (5.4 g, 48 mmol). To this solution was added dropwise a THF solution (60 ml) of methylmagnesium bromide (6.6 g, 60 mmol). The reaction proceeded quickly at ambient temperature, producing a precipitate of magnesium bromide chloride and color of the solution changing from yellowish brown to deep green. 2-Methylpyridine was yielded quantitatively and absence of unreacted 2-chloropyridine and other coupling products was confirmed by the gas-liquid chromatography.

Measurements. IR spectra were recorded in Nujol on JASCO IR-E (4000—650 cm^{-1}), Hitachi EPI-L (700—200 cm^{-1}) and FIS-3 (400—30 cm^{-1}) spectrophotometers. JEOL JNM C60-HL and PS-100 spectrometers were used to obtain ^{1}H NMR spectra at 60 and 100 MHz, respectively, in CD_2Cl_2 with tetramethylsilane as external reference. ^{13}C NMR spectra were taken in CD_2Cl_2 with a JEOL JNM-FX60 spectrometer at 15.0 MHz. Tetramethylsilane was used again as external reference. The molecular weight was determined by vapor pressure osmometry in dichloromethane at 25 °C with an instrument manufactured by Knauer in Berlin, Germany. Mass spectra were measured with a Hitachi GC-mass-spectrometer M-52 and gas chromatography was performed on a Varian Aerograph Model 920 through a column of Silicon OV 17 with helium as a carrier gas. The injection temperature was 100 °C.

Results and Discussion

Tetrakis(triphenylphosphine)nickel(0) has frequently been used as a starting material for preparation of the aryl and other organonickel compounds, and proved now to react readily with halogenated nitrogen heterocycles such as 2- and 3-halogenopyridines, 2,6- and 3,5-dichloropyridines, 2-chloro-6-methoxypyridine, 2-chloropyrazine, and 8-chloroquinoline. In each case the reaction occurred at room temperature and the time necessary for completion of reaction increased in the sequence of 2-bromopyridine<2-chloropyrazine ≈ 2-chloropyridine < 2-chloro-6-methoxypyridine ≈ 2,6-dichloropyridine < 3-chloropyridine < 3,5-dichloropyridine, indicating that the reactivity of pyridine at the C^2 position with nickel(0) is appreciably higher than at the C^3 position. 2-Chlorothiophene did not react with $Ni(PPh_3)_4$. 2-Chlorobenzothiazole did react, but gave no organonickel compound, producing dichlorobis(triphenylphosphine)nickel(II). The reaction of tetrakis(triphenyl phosphite)nickel(0) with 2-chloropyridine was examined, but refluxing in toluene for 10 h showed no sign of reaction.

Characterization of the Di-μ-halogeno-bis(σ-pyridyl)bis-(triphenylphosphine)dinickel(II) Complexes. The analytical and molecular weight data of these complexes are collected in Table 1. The 3-pyridyl complex (**3**) is less stable than the 2-pyridyl complexes and decomposes gradually on exposure to air, thus giving unsatisfactory analysis. The complexes in Table 1 are all diamagnetic and have the square-planar structure, indicating the effect of π-bonding between the carbon-bonded pyridine ring and the nickel(II) ion, since dichlorobis(triphenylphosphine)nickel(II) has a tetrahedral structure.[15]

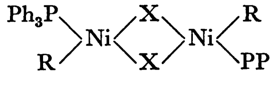
The molecular weight data indicate that all complexes except **6** are dinuclear. Characteristic IR data for these complexes are summarized in Tables 2 and

TABLE 1. ANALYTICAL DATA FOR THE σ-PYRIDYL NICKEL(II) COMPLEXES

Complex		Found (Calcd)			
		C(%)	H(%)	N(%)	mol wt[a)]
$[NiCl(C_5H_4N\text{-}C^2)(PPh_3)]_2$	**1a**	62.67 (63.57)	4.57 (4.40)	3.31 (3.23)	829 (869)
$[NiBr(C_5H_4N\text{-}C^2)(PPh_3)]_2$	**1b**	58.04 (57.67)	4.10 (4.00)	2.99 (2.93)	790 (958)
$[NiI(C_5H_4N\text{-}C^2)(PPh_3)]_2$	**1c**	51.68 (52.52)	3.65 (3.64)	2.63 (2.66)	840 (1052)
$[NiCl(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]_2$	**2a**	58.41 (58.90)	3.84 (3.87)	3.11 (2.99)	947 (940)
$[NiCl(C_5H_3(5\text{-}Cl)N\text{-}C^3)(PPh_3)]_2$	**2b**	59.55 (58.90)	4.10 (3.87)	3.20 (2.99)	890 (940)
$[NiCl(C_5H_4N\text{-}C^3)(PPh_3)]_2$	**3**	61.54 (63.57)	4.35 (4.40)	3.12 (3.23)	
$[NiCl(C_4H_3N_2\text{-}C^2)(PPh_3)]_2$	**4**	59.78 (60.67)	4.06 (4.16)	6.24 (6.43)	857 (871)
$[NiCl(C_5H_3(6\text{-}CH_3O)N\text{-}C^2)(PPh_3)]_2$	**5**	62.04 (62.05)	4.48 (4.56)	3.00 (3.01)	881 (927)
$[NiCl(C_9H_6N\text{-}C^8)(PPh_3)_2]$	**6**	72.11 (72.36)	4·80 (4.86)	1.77 (1.88)	710 (747)
$[NiN_3(C_5H_3(6\text{-}CH_3O)N\text{-}C^2)(PPh_3)]_2$	**7a**	60.73 (61.12)	4.47 (4.59)	11.75 (11.88)	910 (943)
$[NiNCO(C_5H_3(6\text{-}CH_3O)N\text{-}C^2)(PPh_3)]_2$	**7b**	62.46 (63.67)	4.43 (4.59)	5.89 (5.94)	940 (943)
$[NiNCS(C_5H_3(6\text{-}CH_3O)N\text{-}C^2)(PPh_3)]_2$	**7c**	61.44 (61.57)	4.32 (4.44)	5.80 (5.74)	970 (975)
$[NiNCSe(C_5H_3(6\text{-}CH_3O)N\text{-}C^2)(PPh_3)]_2$	**7d**	55.11 (56.17)	3.90 (4.05)	5.19 (5.24)	990 (1069)
$[NiN_3(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]_2$	**7a′**	56.57 (56.52)	3.78 (3.96)	12.55 (11·46)	923 (951)
$[NiNCO(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]_2$	**7b′**	60.68 (60.62)	3.88 (3.82)	6.04 (5.89)	924 (951)
$[NiNCS(C_5H_3(6\text{-}Cl)N\text{-}C^2)(PPh_3)]_2$	**7c′**	58.44 (58.64)	3.68 (3.69)	5.74 (5.70)	956 (983)
$[Ni(acac)(C_5H_3(6\text{-}Cl)N\text{-}C^2)]_2$	**8**	44.19 (44.43)	4.10 (3.72)	4.82 (5.18)	528 (541)

a) In dichloromethane at 25 °C.

3. As is seen in Table 2, two distinct ν(Ni–X) bands are observed for each complex and the frequencies are reasonable for the bridging halides.[16,17)] The IR spectra in the lower frequency region also exhibit one band each at about 340 cm^{-1} which is assigned unambiguously to the ν(Ni–P) vibration. These IR-spectral patterns strongly support the following C_{2h} *trans* structure for the dinuclear complexes.[18)]



Since the alkyl and aryl ligands are usually considered to exert a stronger *trans* influence than the tertiary phosphines,[19)] the higher frequency one of the two ν(Ni–X) bands may be assigned to the vibration of the Ni–X bond *trans* to triphenylphosphine. The ν(Ni–Cl) frequencies (289 and 248 cm^{-1}) for **1a** are similar to but appreciably lower than those (302 and 280 cm^{-1}) for $[NiCl(CH_3)(PMe_3)]_2$,[17)] probably indicating a stronger *trans* influence of the 2-pyridyl ligand than that of the methyl group. The ν(Ni–Cl):ν(Ni–Br):ν(Ni–I) ratio (1:0.67:0.53) for **1a**, **1b**, and **1c** is appreciably different from the values found for other halogenonickel(II) complexes, *e.g.* 1:0.83:0.70 for NiX_2(1,2-bis(diphenylphosphino)ethane).[20)] The reason is not certain why the halogen-discriminating ability of nickel(II) is enhanced in the present complexes. As is expected from the order of *trans* influence of halide ions, the ν(Ni–P) frequencies slightly decrease in the sequence of **1a**>**1b**>**1c**.

TABLE 2. DECOMPOSITION TEMPERATURES AND SOME FIR DATA

Complex	Dec. temp °C	ν(Ni-X) cm^{-1}		ν(Ni-P) cm^{-1}
1a	187	289 s	248 s	338 s
1b	170	191 s	170 m	337 s
1c	160	152 m	134 m	329 s
2a	194	305 m	250 m	355 m
2b	140	283 s	246 s	337 w
3	124	310 w	245 w	360 s
4	193	290 s	245 m	335 m
5	187	290 s	250 s	340 w
6	170	352 s		290 m

When 2,6- or 3,5-dichloropyridine is used as a reactant, it may be expected to react with two molecules of tetrakis(triphenylphosphine)nickel(0) to afford a dinuclear complex in which the pyridine links to nickel atoms *via* two ring carbons. In reality compounds **2a** and **2b** were obtained, which showed no sign of reaction with another nickel(0) compound. On coordination to a metal atom, electron density of the pyridine ring may be increased by the π-bonding so as to prevent the oxidative addition to another nickel(0).

All complexes listed in Table 2 except compounds **2b** and **3** are stable on long-time exposure to air and their decomposition temperatures are higher than that of *trans*-chloro(phenyl)bis(triphenylphosphine)nickel(II) (122—3 °C).[2b)] The thermal stability diminishes in the sequence of Cl>Br>I and 6-chloro-2-pyridyl≈2-pyrazinyl>2-pyridyl≈6-methoxy-2-pyridyl>5-chloro-3-pyridyl>3-pyridyl. The former sequence suggests the operation of antisymbiotic effect,[21)] increasing softness of the halide ions weakening the *trans* Ni–C bond. Similarly, the lowest π^* level becomes higher[22)] and the M→L π-bonding ability decreases in the sequence of pyrazinyl>pyridyl>phenyl. Instability of the 3-pyridyl complexes relative to the 2-pyridyl complexes may be caused by the larger electron density at the 3-position of pyridine than at the 2-position[23)] which lowers the acceptor ability.

Data of ^{1}H NMR spectra for the chloro complexes are included in Table 4. In each case the ring protons

Table 3. Characteristic IR data for the μ-pseudohalogeno complexes[a)]

Complex	ν(CN) or ν_a(NNN)	ν(CY) or ν_s(NNN)	δ(NCY) or δ(NNN)	ν(Ni-N)	ν(Ni-Y)	ν(Ni-P)
7a	2060 s	1340 w	590 w	410 m	398 m	343 w
7b	2226 s	1332 m	598 m	398 m	373 m	333 w
7c	2100 vs	b)	b)	400 m	347 w	337 w
7d	2110 vs	620 w, 590 w	b)	367 m	b)	320 m
7a′	2080 vs	1347 m	585 w	413 m	413 m	323 m
7b′	2245 vs	1345 m	602 m	415 m	375 m	329 m
7c′	2100 vs	b)	b)	395 m	350 m	323 m

a) Y=O, S, or Se. b) Indiscernible.

Table 4. Proton chemical shifts from external TMS in dichloromethane

	Hetero-ring proton at the position				Phenyl ring proton at the position		Methyl proton
	3	4	5	6	*meta* and *para*	*ortho*	
1a	6.33 m	6.79 m	6.27 m	8.57 m	7.30 m	7.90 m	
2a	6.45 d	6.21 t	6.65 d		7.31 m	8.03 m	
4	8.52 m		a)	a)	7.34 m	7.88 m	
5		(6.16 m, 5.76 m)[b)]			7.35 m	8.16 m	4.00 s
6[c)]	a)	a)			(7.50 m)[b)]		
7a	6.27 m	5.83 m	6.27 m		7.35 m	7.95 m	4.05 s
7b	6.29 m	5.82 m	6.29 m		7.40 m	8.04 m	4.02 s
7c	6.35 s	5.84 m	6.35 s		7.47 m	8.00 m	4.04 s
7d	6.33 s	5.86 m	6.33 s		7.46 m	7.96 m	4.06 s
7c′	6.72 d	6.34 t	6.54 d		7.50 m	7.90 m	
8	7.30 d	6.70 t	7.00 d				1.90 s, 2.00 s

s=singlet, d=doublet, t=triplet, m=multiplet

a) Masked by the signals of phenyl protons. b) Unassignable. c) H^2 and H^6 resonate at 8.82(m) and 6.75(m) ppm, respectively.

of triphenylphosphine resonate as two multiplets with the area ratio of 3:2 in the 7.30—7.50 and 7.88—8.16 ppm regions, respectively. The higher-field signal is assigned to the *meta* and *para* protons and the lower-field one to the *ortho* protons.[24)] The pyridine-ring protons of **1a** exhibit an ABCX-type signals at 6.27, 6.33, 6.79, and 8.57 ppm, showing large up-field shifts as compared with those at 7.18 (H^3), 7.55 (H^4), and 8.69(H^2) ppm for uncoordinated pyridine. The M→L π-bonding in the present complexes may be much more extensive than in *trans*-$NiBr(C_6H_5)(PEt_3)_2$, since the chemical shifts of the phenyl protons (6.90 and 7.40 ppm) in this complex are not so different from that of benzene (7.15 ppm).[25)]

When H^2 of pyridine is substituted by an electron-releasing group, similar up-field shifts of the ring proton signals are observed. Thus ring protons of 2-methylpyridine resonate at 6.92 (H^5), 7.00 (H^3), 7.43 (H^4), and 8.51 (H^6) ppm and those of 2-aminopyridine at 6.60 (H^5), 6.70 (H^3), 7.44 (H^4), and 8.11 (H^6) ppm.[26)] By reference to these data the pyridyl proton signals were assigned as shown in Table 4. A similar trend was also observed for $[Co(CN)_5(2\text{-pyridyl})]^{3-}$ but the up-field shifts are not so large as for the present complexes.[9)]

As is seen in Fig. 1, the pyridine-ring protons of **2a** show a triplet at 6.21 ppm and two doublets at 6.45 and 6.65 ppm. They are tentatively assigned to H^4, H^3, and H^5, respectively, on the assumption of the first-order ABC spin system.[27)] In the case of uncoordinated 2-chloropyridine, signals for the corresponding protons are observed at 7.83, 7.39, and 7.49 ppm, respectively.[26)] A great deal of the up-field shifts of the ring-proton signals on coordination are again noted, the shift at H^4 (*meta* position from the metal) being the largest. Table 5 collects the ^{13}C NMR data for complex **2a** together with those for triphenylphosphine[28)] and 2-chloropyridine[29)] for

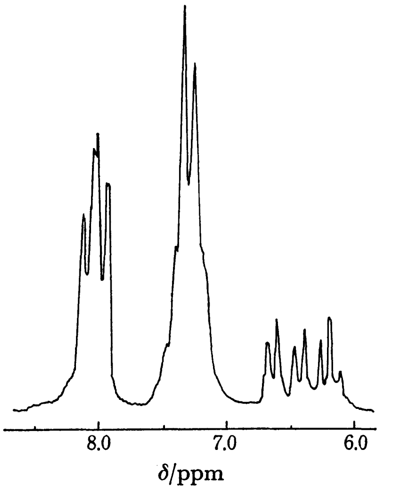
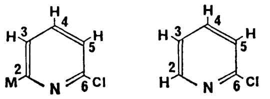


Fig. 1. The ^1H NMR spectrum of $[NiCl(C_5H_3(6\text{-}Cl)\text{-}N\text{-}C^2)(PPh_3)]_2$ (**2a**) in CD_2Cl_2 with external TMS.

Table 5. ^{13}C NMR data



Compound	Chemical shift (δ/ppm)					Coupling constant/Hz
$P(C_6H_5)_3$	C^1	C^2	C^3	C^4		$J(P\text{-}C^1)=21$, $J(P\text{-}C^2)=20$
	138.3	134.4	129.2	129.3		$J(P\text{-}C^3)=7$, $J(P\text{-}C^4)<1$
$2\text{-}Cl\text{-}C_5H_4N$[a)]	C^2	C^3	C^4	C^5	C^6	
	151.1	123.9	138.5	122.4	149.7	
2a Phenyl carbon	C^1	C^2	C^3	C^4		$J(P\text{-}C^1)\simeq 20$, $J(P\text{-}C^2)=12$
	134.2	135.7	128.5	130.5		$J(P\text{-}C^3)=10$, $J(P\text{-}C^4)=0$
2a Pyridyl carbon	C^2	C^3	C^4	C^5	C^6	
	131.8	118.8	128.7	128.1	130.5	

a) Ring carbons are numbered by reference to the complex as above.

comparison. Tentative assignments are given on the basis of the relative intensity and the J(P–C) value of each carbon and also by reference to the above literature data. In a similar manner as the proton resonances, the pyridine-ring carbons exhibit remarkable up-field shifts on coordination.

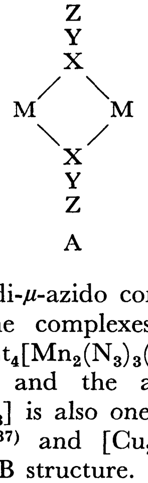
The pyridine-ring protons of compound **5** show two broad signals at 5.76 and 6.16 ppm, the methoxy protons resonating at 4.00 ppm. The corresponding proton signals for uncoordinated 2-methoxypyridine are observed at 6.62 (H^3), 7.40 (H^4), 6.70 (H^5), and 3.84 (CH_3) ppm. It is noteworthy that the methoxy protons show a down-field shift, while the pyridine-ring protons up-field shifts on coordination.

*Properties of Chloro(8-quinolyl)bis(triphenylphosphine)-nickel(II) (**6**).* As stated already only 8-chloroquinoline gave the mononuclear complex **6** on reaction with $Ni(PPh_3)_4$. Complex **6** exhibits a single ν(Ni–Cl) band at 350 cm^{-1} and a ν(Ni–P) band at about 290 cm^{-1}. The ν(Ni–Cl) frequency is quite similar to those observed for the *trans*-$NiCl(aryl)(PR_3)_2$ complexes,[2b,5] and the ν(Ni–P) frequency is a little higher than that observed for *trans*-$NiCl_2(PEt_3)_2$ (273.4 cm^{-1})[30] probably due to the weaker *trans* influence of PPh_3 as compared to PEt_3.[19] Thus complex **6** is considered to have the *trans* structure. It is stable in the air and the decomposition temperature (170 °C) is much higher than that of *trans*-$NiCl(C_6H_5)(PPh_3)_2$ (122—123 °C).[2b] The remarkable stability of **6** may be caused partly by the "*ortho* effect"[3] exerted by the fused pyridine ring in the 8-quinolyl ligand.

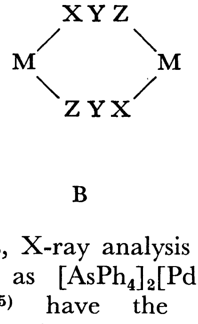
Proton NMR data for **6** are included in Table 4. In contrast with other dinuclear complexes, **6** exhibits a broad signal at about 7.50 ppm due to the phenyl protons. Of the quinoline-ring protons H^2 and H^6 resonate at 8.82 and 6.75 ppm, respectively, other proton signals being masked by those of the phenyl protons. Compared with the chemical shifts of H^2 (8.81 ppm) and H^6 (7.44 ppm) of uncoordinated quinoline,[26] the signal of H^6 which is in the *meta* position from the metal shows a remarkable up-field shift on ligation.

Characterization of the Di-μ-pseudohalogeno-bis(σ-pyridyl)-bis(triphenylphosphine)dinickel(II) Complexes. The bridging chloride ions in complexes **2a** and **5** were readily replaced by the azide, cyanate, thiocyanate, and selenocyanate ions to afford two series of compounds **7** in a mixture of dichloromethane and methanol at room temperature, the yields decreasing in the sequence of $SCN^- > OCN^- > N_3^-$ for both series. The analytical and molecular weight data listed in Table 1 together with the diamagnetic behavior indicate that the dinuclear square-planar structure is preserved in these complexes. Many dinuclear transition metal complexes containing pseudohalides as the bridging ligands have been prepared so far,[31–33] but no example of the square-planar nickel(II) complexes of this kind has been reported to our knowledge.

Of various bridging modes of the pseudohalide anions, the "one-end" bridge (A) and the "end-to-end" bridge (B) are most widely recognized. In the case



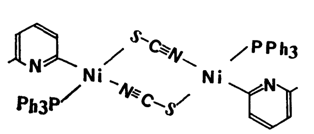
A



B

of the di-μ-azido complexes, X-ray analysis revealed that some complexes such as $[AsPh_4]_2[Pd_2(N_3)_6]$[34] and $NEt_4[Mn_2(N_3)_3(CO)_6]$[35] have the type A structure and the azide ion in $[Rh_2N_3(\eta^5\text{-}C_5Me_5)\text{-}(N_3C_4F_6)_3]$ is also one-end bridging,[36] while $[Cu(N_3)\text{-}(PPh_3)_2]_2$[37] and $[Cu_2(N_3)_2(Me_5dien)_2](BPh_4)_2$[38] have the type B structure. However both of the di-μ-azido structures have the local D_{2h} symmetry and it is impossible to distinguish between them only from the IR-spectral information. The cyanate ion usually coordinates to transition metals through the nitrogen atom,[31,33] and only one pair of linkage isomers has been reported in the solid state.[39] When the cyanate ion is involved in a dinuclear complex, one-end bridging at the nitrogen atom (type A) is common and the type B bridging has been found only in $[Ni_2(NCO)_2(tren)_2](BPh_4)_2$,[40] where tren is $N(CH_2\text{-}CH_2NH_2)_3$, and $(C_6H_5)_3TeNCO\cdot 0.5CHCl_3$.[41] In the case of thiocyanate and selenocyanate ions, however, the bridging mode of type B is usually preferred to type A,[31,33] although the one-end bridging both at nitrogen[42] and sulfur[43] atoms has been exemplified.

Each of compounds **7a**—**7d** containing the 6-methoxy-2-pyridyl ligand exhibits a single sharp signal assignable to the methyl protons, indicating that neither geometrical nor linkage isomers are involved in each case. As is seen in Table 4 the pattern of ^{1}H NMR spectra for **7a**—**7d** and the chemical shifts of phenyl and pyridyl ring protons in these complexes show a striking resemblance to each other irrespective of the nature of the pseudohalide anions, suggesting the existence of a common bridging mode. We would like to tentatively assume the end-to-end bridging with the *trans* configuration (C). The IR spectral data in Table 3 are not diagnostic but conform to the presumed structure.



C

Characterization of Compound 8. The analytical and molecular weight data in Table 1 indicate that compound **8** is dinuclear. The ν(C═O) and ν(C═C═C) bands are observed at 1565 and 1514 cm^{-1}, respectively, resembling those of $Ni_3(acac)_6$ at 1598 and 1520 cm^{-1}. Figure 2 shows the ^{1}H NMR spectrum of **8** in CD_2Cl_2. Two kinds of methyl signals are observed at 1.90 and 2.00 ppm. The pyridyl protons resonate at 6.70, 7.00, and 7.30 ppm. The coupling constants to each other are equal to those for **2a**, but the down-field shifts of these signals are remarkable as compared with those of **2a** although they still exist in higher field than proton signals of uncoordinated 2-chloropyridine. All pieces of the spectral information well conform to the proposed structure. To our knowledge this is the first example of the square-planar NiO_3C-type complexes, although the NiO_2CP-type complexes such as $NiC_2H_5(acac)PPh_3$[44] have been reported. Again the strong effect of π-bonding between the pyridyl ligand and the nickel ion upon stabilizing the σ-carbon-bonded complex is noted.

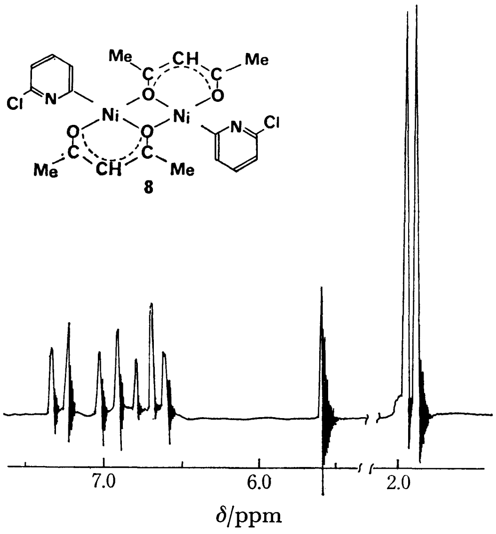
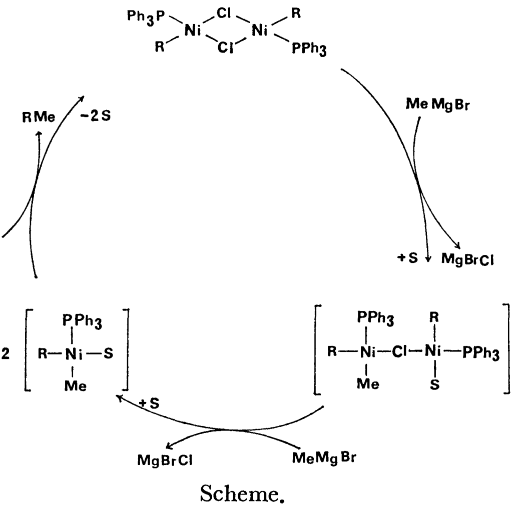


Fig. 2. The ^{1}H NMR spectrum of $[Ni(acac)(C_5H_3\text{-}(6\text{-}Cl)N\text{-}C^2)]_2$ (**8**) in CD_2Cl_2 with external TMS.

Reactions of the σ-Pyridyl Complexes. Reactions of **1** with excess triphenylphosphine, thiourea, and pyridine were tried in vain at room temperature, ending in recovery of **1**. Refluxing of a solution of **1a** in neat pyridine for 2 h gave dichlorobis(pyridine)-nickel(II) in a 40% yield. Complex **6** reacted with acetylacetone to produce $Ni(acac)_2(C_9H_7N)_2$ in a 55% yield. Found: C, 64.78; H, 5.46; N, 5.19%. Calcd for $C_{28}H_{28}N_2O_4Ni$: C, 65.27; H, 5.48; N,5.44%. Presumably acetylacetone acted as an acid to split the nickel–quinolyl bond, the conjugate base (acac anion) replacing the chloride ion. It is noteworthy that bis(acetylacetonato)nickel(II) preferred quinoline to triphenylphosphine as a base in the adduct formation.

The reactions of bases such as pyridine and triphenylphosphine with **8** to break the dinuclear structure were unsuccessful at ambient temperature, but refluxing in a mixture of dichloromethane and methanol effected decomposition of **8** to yield unidentified products. When triphenyl phosphite was employed as a base, refluxing in methanol gave rise to 6,6′-dichloro-2,2′-bipyridine and tetrakis(triphenyl phosphite)nickel(0). Reductive elimination has occurred to yield a homocoupled product and the nickel(0) complex. The other product containing the acetylacetonate moiety has not been identified.

When Grignard reagents RMgBr (R=CH_3 or C_6H_5) and 2-pyridyllithium were reacted with **1a**, the diorganonickel complexes were not obtained, but instead 2-methylpyridine was yielded in the case of methylmagnesium bromide. On the contrary to the extraordinary stability of the σ-pyridyl nickel(II) complexes, the diorganonickel complex must be unstable, immediately undergoing a coupling reaction. As was described in the Experimental section, complex **1a** was found to be an excellent catalyst for the cross coupling of 2-chloropyridine with methylmagnesium bromide in THF at ambient temperature to produce 2-methylpyridine quantitatively. The pathway of the catalytic turn-over may be visualized by the proposed Scheme. The intermediates in brackets have not



Scheme.

been isolated but just presumed. A molecule S is used for bookkeeping of the coordination number and may be either the solvent or *N*-bonded 2-chloropyridine.

Morrell and Kochi[25] prepared *trans*-methylphenyl-(and *o*-tolyl)bis(triethylphosphine)nickel(II) and determined the rates of reductive elimination to yield toluene and *o*-xylene, respectively. These rates were found to be too slow to allow for a catalytic process probably because of the *trans* structure. Oxidative addition of aryl halides to nickel(0) species usually affords trans products, showing no sign of isomerization to either a *cis* isomer or a tetrahedral species.[25] These results offer a trouble to understanding of the cross coupling mechanism. In the present case, on the other hand, the dinuclear structure of **1a** is quite favorable for the catalytic steps, allowing the *cis* arrangement of the two organic ligands as depicted in Scheme.

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